Electrolyte Distributions at Interfaces: Deviations from Gouy-Chapman Theory Due to Liquid Structure

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Results: We demonstrate the importance of liquid structure on ion distributions by carrying out x-ray reflectivity measurements from the liquid-liquid interface between two electrolyte solutions. We demonstrate a method for predicting the measured distributions that is likely to be applicable to other interfaces (liquid-vapor, solid-liquid).

Ion Distributions near Charged Interfaces

Ion distributions near charged interfaces in electrolyte solutions underlie many electrochemical and biological processes, including electron and ion transfer across interfaces.

Some biological examples:

Screening determines forces between charged macromolecules such as polyelectrolytes

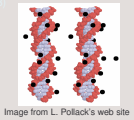
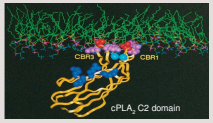
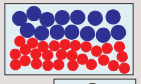


Image from L. Pollack's web site

The interactions between proteins and biomembranes are mediated by multivalent ions

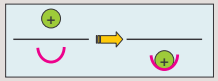


At the liquid-liquid interface:



Effect of ion pairing on chemical reactions and electron transfer

Ion or electron transfer across the interface



Assisted ion transfer at the interface

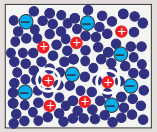
What is the problem?

First, consider the interaction of two ions.

Two isolated point charges:
Coulomb's Law
Electric potential: $\phi = \frac{1}{4\pi\varepsilon_\circ}\frac{q}{r}$

Two point charges in continuum dielectric:
$\phi = \frac{1}{4\pi\varepsilon_\circ\varepsilon_r}\frac{q}{r}$

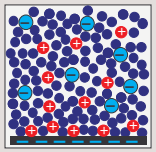
Two charges interacting in continuum dielectric with other point charges:
Debye-Huckel Screening
$\phi = \frac{1}{4\pi\varepsilon_\circ\varepsilon_r}\frac{q}{r}e^{-kr}$



Include Liquid Structure:
Correlations important -
solvent-solvent
solvent-ion
ion-ion

This last picture reveals the complexity of the problem: the liquid structure that arises due to correlations between ions and solvent molecules will influence the interactions between the two ions.

A similar problem occurs when we want to determine the interactions of ions with a charged interface or surface.

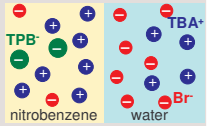


Spatial correlations are important:
solvent-solvent
solvent-ion
ion-ion

Electrified Nitrobenzene/Water Interface

We have chosen to probe ion distributions at the interface between a polar oil and water for two reasons:
(1) the electric field at this interface can be controlled, and
(2) there is nothing besides ions and solvents (such as a solid electrode) that might influence the ion distributions.

We use a common ion in both phases:
ion partitioning produces an electric potential across the interface.



We fix the initial solution concentration of TBATPB at 0.01 M in nitrobenzene, then vary the TBABr concentration to vary the electric potential across the interface.

Gouy-Chapman Theory

Gouy-Chapman theory is often used to describe experiments whose results depend upon ion distributions. Sometimes it works well, sometimes not.

This theory describes the ion distributions by using Poisson's equation $\frac{d^2\phi}{dz^2} = -\frac{\rho(z)}{\varepsilon}$ (dependence of the electric potential on the charge distribution).

The charge is then Boltzmann distributed to yield the Poisson-Boltzmann equation

$$\frac{d^2\phi}{dz^2} = -\frac{1}{\varepsilon}\sum_{ions} c_i^o \exp(-e_i\phi(z)/kT)$$

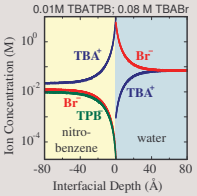
Gouy-Chapman theory assumes point charges in a continuum solvent. It depends upon the interaction of the charges with the mean field of all other charges, and neglects liquid structure and correlations previously mentioned.

The failure of Gouy-Chapman theory to describe our data will lead to a modification of the Poisson-Boltzmann equation that incorporates the liquid structure and describes our data.

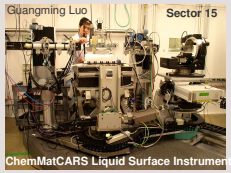
Measuring the Ion Distributions

What does the Gouy-Chapman theory predict for the distributions of ions in our samples?

This plot shows that there is an electrical double layer on each side of the interface. Since the electric potential of the water is negative with respect to the nitrobenzene phase, Br^- ions are expelled to the water side of the interface and TBA^+ ions to the nitrobenzene side.



From the ion distributions, we calculate the electron density distribution, then the x-ray reflectivity, which we compare to measurements from Sector 15 (ChemMatCARS) of the Advanced Photon Source (USA). X-ray reflectivity probes the electron density as a function of depth into the liquid/liquid interface.



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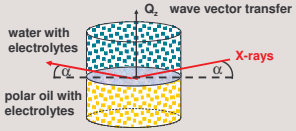


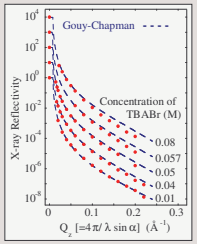
Reflectivity from Liquid-Liquid Interface

X-ray Reflectivity Data and the Gouy-Chapman Prediction

After converting the ion distributions calculated from Gouy-Chapman theory to an electron density as a function of interfacial depth using:

1) ion sizes from radial distribution functions determined by MD simulations and other measurements, and
2) thermal fluctuations of the interface determined by capillary wave theory,

we calculate the x-ray reflectivity and compare to our measurements (see below).



The Gouy-Chapman calculation differs significantly from our data, by up to 25 standard deviations.

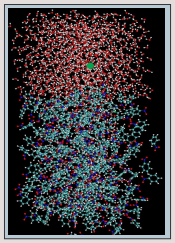
Potential of Mean Force and Poisson-Boltzmann Equation
The Effect of Liquid Structure on the Ion Distributions

To understand why the Gouy-Chapman theory failed, let us reconsider the Poisson-Boltzmann Equation

$$\frac{d^2}{dz^2}\phi(z) = -\frac{1}{\varepsilon}\sum_i e_i c_i^o \exp[-E_i(z)/k_BT] \qquad E_i(z) \text{ is the ion energy}$$

In the Gouy-Chapman theory, the ion energy is taken as just the electrostatic energy: $E_i(z) = e_i\phi(z)$. This neglects the liquid structure.

Looking at the simulation to the right (water on top, nitrobenzene on bottom, and an exaggerated green sphere at the position of one Br^- ion), it is sensible to expect that the ion will interact and be correlated with the surrounding solvent molecules. These interactions will vary with the interfacial depth of the ion. These interactions, in addition to those of the electrostatic field, will influence the distribution of the ion with depth.

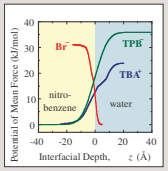


We approximate these interactions by an MD simulation of the Potential of Mean Force of a single ion. The total energy of each ion in our sample is the sum of the electrostatic part plus the Potential of Mean Force $f_i(z)$.

$$E_i(z) = e_i\phi(z) + f_i(z)$$

When placed in the Poisson-Boltzmann equation (above), this expression accounts for solvent-solvent, ion-solvent interactions and correlations, ion and solvent sizes, but not for ion-ion correlations.

Potential of Mean Force (PMF) and Ion Distributions

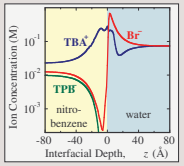


Potential of Mean Force:
Br^- and TBA^+ from MD simulations
TPB^- from analytic expression.
0.08M TBABr in water
0.01M TBATPB in nitrobenzene
TBABr: tetrabutyl ammonium bromide
TBATPB: tetrabutyl ammonium tetraphenyl borate

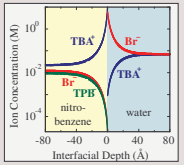
These curves are essentially a free energy profile for the ions, excluding the mean electrostatic field.

Influence of the Liquid Structure, on Ion Distributions

From PMF theory

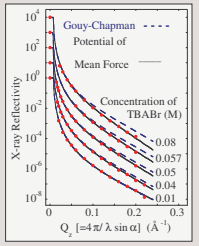


From Gouy-Chapman Theory



Note the reduced concentration at the interface and the structure in the TBA^+ ion distribution.
Both effects are due to the finite size of ions.

Predictions of the Potential of Mean Force Theory Match the X-ray Data



Prediction from Potential of Mean Force matches the x-ray data.

No adjustable parameters and no fitting in this analysis.

Conclusions

The importance of liquid structure on ion distributions at interfaces between electrolyte solutions has been demonstrated.

This work provides a straightforward method to include the effects of liquid structure on ion distributions by using MD simulations of the potential of mean force in the Poisson-Boltzmann equation -- requires negligible ion-ion correlations (true for this sample).

This work also provides a method to test a potential of mean force produced by either analytical theory or simulation.

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